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[There are no amendments to this patent.]

### Abstract

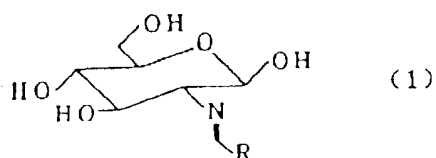
#### Objective

The present invention provides glucosamine derivatives substituted with a fragrance compound of the following formula (1) not described in the literature, and also provides a

# Claims

1. Substituted glucosamine derivative of the following formula (1):

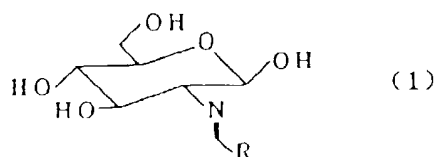
[Structure 1]



(in the formula, R represents an aliphatic aldehyde residue, an aromatic aldehyde residue, or an alicyclic aldehyde residue).

2. A long-lasting fragrance composition characterized by containing as an active ingredient a substituted glucosamine derivative of the following formula (1):

[Structure 2]



(in the formula, R represents an aliphatic aldehyde residue, an aromatic aldehyde residue, or an alicyclic aldehyde residue).

the long-lasting fragrance of the derivative or flavor of the compound gathered much attention, and a number of patent applications were submitted for inventions. Research on glycoside fragrance, a precursor of a fragrance compound, was undertaken by the inventors, and an application for a patent was submitted. Patent applications were submitted for fragrance-reinforcing agents made from plants characterized by containing glycoside fragrance as an active ingredient (Japanese Kokai Patent Application Hei 6[1994]-336401) and aromatic composition gradually releasing fragrance, containing fragrance glycoside as an active ingredient, and used for humans (Japanese Patent Application No. Hei 5[1993]-307309). The purposes of the prior [patent] applications were to provide a long-lasting fragrance composition whose fragrance or flavor lasted for a long time and which gradually released the fragrance compound when the glycoside bonds of the glycoside are cut due to the contact enzymes present in the plant body, bacteria always present on human skin, or sweat secreted by the human body.

[0003]

Problems to be solved by the invention

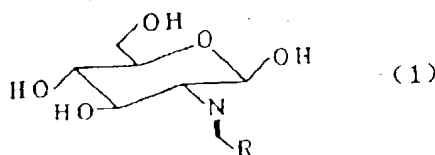
Because consumer preference is widely varied, a variety of products is desired. Especially, in the food and beverage or the fragrance and cosmetics field, development of a variety of foods and beverages or of fragrances and cosmetics corresponding to the preference of consumers is in demand. Because [present] fragrances which are raw materials and are made from fragrance compounds for which patent applications have been submitted, have

[0006]

Means to solve the problems

The present invention provides a long-lasting fragrance composition containing a substituted glucosamine derivative of the following formula (1):

[Structure 4]



(in the formula, R is the same as above) and a long-lasting fragrance composition characterized by containing the derivative as an active ingredient.

[0007]

Application mode of the invention

A compound of formula (1) used in the present invention can be easily made by carrying out reaction of glucosamine chloride of the following formula (2):

hydrochloride or sulfuric acid [sic]. Glucosamine chloride can be easily obtained commercially at a low price. Examples of compounds of formula (2) which can be obtained by the above-mentioned process include glucosamine chloride and glucosamine sulfate.

[0009]

Aldehydes of formula (3), another raw material used in the present invention, are fragrance compounds used as a fragrance material, and are easily obtained commercially at a low price. Examples of compounds of formula (3) include aliphatic aldehydes such as acetaldehyde, isopropyl aldehyde, propyl aldehyde, isobutyraldehyde, butyraldehyde, amyl aldehyde, isoamyl aldehyde, octanal, 3-methyl-1-pentanal, 2-hexanal, 2-heptanal, 3,5,5-trimethylhexanal, undecyl aldehyde, cis-3-hexenal, 6-nonen-1-al, trans-4-decenal, 2,6-nonadien-1-al, homocitronellal, neral, citral, lavandulal, farnesol, hydroxycitronellal, or methylthioacrolein; alicyclic aldehydes such as perilaldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde, 4-(4-methyl-3-penten-1-yl)-3-cyclohexene-1-carboxaldehyde, 3,5-dimethyl-3-cyclohexene-1-carboxaldehyde, perilaldehyde [sic], or furfural; aromatic aldehydes such as benzaldehyde, cumaldehyde, phenyl acetaldehyde, phenylpropyl aldehyde, cinnamaldehyde,  $\alpha$ -amyl cinnamaldehyde, anisaldehyde, vanillin, piperonal, helional, cyclamen aldehyde, lilial, salicyl aldehyde, or hexyl cinnamaldehyde.

[0013]

## ① 置換グルコサミン誘導体「(1) 化合物」

- ③  $\alpha$ -3-ヘキセリデン-D-7' グルコサミン  
 ⑤ オクサリデン-D-7' グルコサミン  
 ⑥ シクロオキサリデン-D-7' グルコサミン  
 ⑦ ペンタリデン-D-7' グルコサミン  
 ⑧ 2-フェニルオキサリデン-D-7' グルコサミン  
 ⑨ シンチリデン-D-7' グルコサミン  
 ⑩ シトリデン-D-7' グルコサミン  
 ⑪  $\alpha$ -アミダシンチリデン-D-7' グルコサミン  
 ⑫ 2-メチル-3-(4-ヒドロキシフェニル)プロピリデン-D-7' グルコサミン  
 ⑬ 2, 4-又は3, 5-ジメチル-3-シクロヘキセニルオキサリデン-D-7' グルコサミン  
 ⑭ 7-ヒドロキシシクロオキサリデン-D-7' グルコサミン  
 ⑮ トランス-2-ヘキセニリデン-D-7' グルコサミン  
 ⑯  $\alpha$ -ヒドロニルプロピリデン-D-7' グルコサミン  
 ⑰ 4-(イソプロペニル)-1-シクロヘキセニルオキサリデン-D-7' グルコサミン  
 ⑱ 4-ヒドロキシ-3-メトキシフェニルオキサリデン-D-7' グルコサミン  
 ⑲ 3-メチルプロピリデン-D-7' グルコサミン

## 融点 (°C) ②

- 107 ■ 110°C (分解)  
 100 ■ 103°C (分解)  
 101 ■ 104°C (分解)  
 104 ■ 110°C (分解)  
 105 ■ 107°C (分解)  
 130 ■ 135°C (分解)  
 114 ■ 115°C (分解)  
 126 ■ 128°C (分解)  
 111 ■ 113°C (分解)  
 105 ■ 108°C (分解)  
 104 ■ 106°C (分解)  
 108 ■ 113°C (分解)  
 105 ■ 110°C (分解)  
 117 ■ 120°C (分解)  
 118 ■ 123°C (分解)  
 90 ■ 95°C (分解)

④

so-called aldehyde-like fragrances and flavor, they are always contained in aldehyde-like fragrance compositions. The amount of compound of formula (1) used for a fragrance composition depends on the purpose or the type of fragrance composition. However, it is suitably 0.001-30 wt% of the entire amount of the fragrance composition.

[0015]

A composition having fragrance and flavor and containing a compound of the above-mentioned formula (1) as an active ingredient can be made by the present invention. The composition can be used to provide foods and beverages characterized by containing a compound of formula (1) as a precursor of a fragrance and flavor component, fragrance and cosmetics characterized by containing a compound of formula (1) as a precursor of a fragrance and flavor component, and health products, sanitary products, or medications characterized by containing a compound of formula (1) as a precursor of a fragrance and flavor component.

[0016]

The following foods and beverages containing suitable amounts of compounds of formula (1) having long-lasting fragrance or flavor can be provided: beverages such as fruit juice, wine, dairy drink, or soda; frozen deserts such as ice cream, sorbet, or ice milk; favorite foods or drinks such as Japanese sweets, cake, jam, chewing gum, bread, coffee, cocoa, tea, or green tea; soups such as Japanese soup or regular soup; flavorings or



filtration. The filtered solution was condensed, then ether was added to wash the condensed solution. Citrylidene-D-glucosamine crystals (14.4 g) were made.

Melting point: 114-115°C (decomposition)

Yield: 92.1%

[0018]

### Application Examples 2-8

Synthesis of each substituted glucosamine derivative (compound of formula (1))

Each substituted glucosamine derivative was synthesized by the same production method used in Application Example 1. The results are shown in Table I.

[0019]

Table I

No.	①式(3)化合物	①式(2)化合物	①式(1)化合物	②収率(%)
2	③	アスコシ塩酸塩	外αリヂン-D-アスコシ	43.6
3	④	アスコシ塩酸塩	αリヂン-D-アスコシ	33.3%
4	⑤	アスコシ硫酸塩	αリヂン-D-アスコシ	24
5	⑥	アスコシ塩酸塩	αリヂン-D-アスコシ	20.1
6	⑦	アスコシ硫酸塩	αリヂン-D-アスコシ	45.2
7	⑧	アスコシ塩酸塩	2-アスコシリヂン-D-アスコシ	39
8	⑨	アスコシ硫酸塩	2,1-又は3,5-リヂン-4-アスコシ	35.5%

separately made. Comparative product a (about 0.5 mL) was applied to the left upper arm of a panel member, and the product of the present invention 1 (about 5 mL) was applied to the right upper arm of the same panel member. Variation in fragrance maintenance on each panel member was compared by follow-up observation. The results are shown in Table II. The following evaluation symbols were used:

- : no generation of citral fragrance was observed
- ±: slight generation of citral fragrance was observed
- +: generation of citral fragrance was observed
- ++: significant generation of citral fragrance was observed
- +++: excessive generation of citral fragrance was observed.

[0021]

Table II

① 経過時間	② 滴下時	③ 6時間後	③ 12時間後	④ 1日後	④ 2日後
⑤ 比較品 1	- - -	+	=	-	-
⑥ 本発明品 1	=	- +	+ - -	+ + +	+ -

Key: 1 Time  
 2 During dropwise application  
 3 After [blank] hours  
 4 After [blank] days  
 5 Comparative product 1  
 6 Product 1 of the present invention

enzymes present in the plant body, or bacteria always present on human skin.